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Engineering and Microstructures Characteristics of Low Calcium Fly Ash Based Geopolymer Concrete

Akram S. Mahmoud[1] & Ganjeena J. Khoshnaw[2] & Faten I. Mahmood[3]

[1]Civil Engineering Department, Engineering College, University of Anbar, Ramadi, Iraq
[2]Erbil Technical institute, Erbil Polytechnic University, Erbil, Iraq
[3]Civil Engineering Department, Engineering College, University of Anbar, Iraq
Correspondence: Akram S. Mahmoud, University of Anbar, Ramadi, Iraq.
Email: dr.akramsh1@gmail.com

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Abstract: This paper reports an experimental study on some mechanical properties and durability characteristics for geopolymer concrete. The mechanical properties were (compressive strength, splitting tensile strength and bonding strength). While the durability characteristics included (permeability, water absorption and exposure to sulphate attack). Also study in-depth microstructure of concrete by the SEM test. All these tests conducted for both geopolymer and normal concrete at 28 days, to show the difference in behavior for the tow concretes. Results show that the compressive strength for geopolymer concrete gain most of its strength at early age as compared with normal concrete, also the results indicate that the bond performance of geopolymer concrete higher than normal concrete by 18.7% and thus proves its application for construction. Geopolymer concrete have good durability comparison with normal concrete, it has shown less permeability, water absorption than normal concrete with high resistance to sulphate attack compared with normal concrete. In addition to that SEM test results show difference in microstructure between geopolymer and normal concrete.

Keywords: Geopolymer Concrete, Durability, Bonding Strength, SEM

1. Introduction

Environmental pollution is one of the major problems today. Manufacture of O.P.C produce 1 ton of CO_2 for all 1 tone of O.P.C (Davidovits, 1994; McCaffrey, 2002; Mehta, 2001; Malhotra, 2002). For this reason an attention is given to industrial waste utilization to building construction due to their advantages of greenhouse gases reduction from Portland cement production. Fly ash is produced as a residual by the combustion of coal. Due to its availability worldwide, disposal remains a challenge. Sustainable construction practice aims at utilizing these waste materials as construction materials. To save the environment from global warming and to prevent further depletion of natural resources, Geopolymer concrete (G.P.C) is an alternative as it totally replaces cement with waste materials such as fly ash.

Geopolymer concrete consists of materials of geological origin or by – product materials such as fly ash that is rich in silicon and aluminum (Davidovits, 1999). The name geopolymer was formed by a French Professor Davidovits in 1978 to represent a broad range of materials characterized by networks of inorganic molecules (Geopolymer Institute, 2010). The geopolymers depend on thermally activated natural materials like Metakaolinite or industrial byproducts like fly ash or slag to provide a source of silicon (Si) and aluminum (Al). These Silicon and Aluminum is dissolved in an alkaline activating solution and subsequently polymerizes into molecular chains and become the binder. In geopolymer concrete water is not involved in the chemical reaction of geopolymer concrete and instead water is expelled during curing and subsequent drying. This is in contrast to the hydration reactions that occur when Portland cement is mixed with water, which produce the primary hydration products calcium silicate hydrate and calcium hydroxide. This difference has a significant impact on the mechanical and chemical properties of the resulting geopolymer concrete, and also renders it more resistant to heat, water ingress, alkali–aggregate reactivity, and other types of chemical attack (Rangan, 2008). In the case of geopolymers made from fly ash, the role of calcium in these systems is very important, because its presence can result in flash setting and therefore must be carefully controlled (Rangan, 2008). The source material is mixed with an activating solution that provides the alkalinity (sodium hydroxide or potassium hydroxide are often used) needed to liberate the Si and Al and possibly with an additional source of silica (sodium silicate is most commonly used). The temperature during curing is very important, and depending upon the source materials and activating solution, heat often must be applied to facilitate polymerization, although some systems have been developed that are designed to be cured at room temperature (Davidovits, 2008). It can be observed from international researchers that the geopolymer concrete has not been studied much in detail in Iraq. In this work 4 geopolymer concrete mixes with 100% replacement of O.P.C. are studied. The production of geopolymer concrete consist of 75% - 80% by mass of aggregate, which is bounded by a geopolymer paste formed by the reaction of the silicon and aluminum in fly ash with the alkaline liquid made up of sodium hydroxide solution and sodium silicate solution with addition of super plasticizer

2. Objective And Scope

The main objective of this study is evaluated durability properties and bond behavior of geopolymer concrete mixture. In addition to that making workable and high strength geopolymer concrete containing fly ash without use of ordinary Portland cement and to prove if the geopolymer concrete useful in construction application.

3. Significance

This paper aims to reduce the use of ordinary Portland cement and to improve the usage of the other by product materials such as fly ash. This product helps in reducing the carbon emissions caused by the conventional concrete. This also produces high strength concretes with the use of nominal mixes when compared to conventional concrete.

4. Materials Used In Experimental Program

4.1 Cement

Cement used in this study was O.P.C (type I) manufactured by mass cement company in Iraq, this cement conforms to the Iraqi standards (Iraqi Specification, 1984). Table (1) shows chemical composition of cement.

Table 1: Chemical composition of cement (mass %)

SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	L.S.F	L.O.I	I.M
22.20	62.83	5.21	3.17	1.92	2.37	0.86	1.11	1.16

4.2 Fly Ash

Fly ash used in this study was low calcium class F obtained from power station Iskanderun in Turkey this type of fly ash conforms to ASTM C 618 (ASTM, 2005) requirement. Table (2) shows the chemical composition of fly ash as determined by X-Ray fluorescence (XRF) analysis

Table 2: Composition of class f fly ash as determined by (XRF) (mass %)

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	Fe_2O_3	L.O.I
0.08	1.27	25.39	47.69	0.16	0.37	1.56	7.93	0.14	11.72	3.34

4.3 Alkaline Liquid

Sodium silicate solution which is the weight ratio of SiO_2/Na_2O equal to 2.4, Na_2O% 13.4%, SiO_2% 32.5% and water 54.1% and sodium hydroxide that is used in this work in pellet form (NaOH with 99% purity), was dissolved in a distilled water in order to avoid the effect of unknown contaminants in the mixing water

4.4 Super Plasticizer

The type of superplasticizer based on modified sulfonated naphthalene formaldehyde condensate

4.5 Aggregate

Natural sand was used with maximum size 4.75mm having specific gravity 2.67 and the coarse aggregate was crushed gravel with maximum size of 14 mm. The aggregate met Iraqi standard specification (Iraqi Specification, 1984).

5. Experimental Program

5.1 Mixing, Casting and Curing of Geopolymer Concrete

After preparation all ingredients of geopolymer mixes. It can be started to mix the dry material (aggregate and the fly ash) together in a pan mixer for 3 minutes. Then super plasticizer was mixed together with alkaline liquid, to form the final alkaline liquid then added to the dry materials in the mixer and the mixing continued for another 3-4 minutes (Hardjito & Rangan, 2005; Rangan, 2010). The fresh concrete had a cohesive consistency and was shiny in appearance, the mixture was cast in a molds with a manual strokes in addition to a vibrating table. After casting immediately the samples were covered by a film and left in laboratory temperature for the specified rest period (Rangan, 2010). The specimen then cured in an oven at as specified temperature 70°C for a selected period of time 24 hr in accordance with the specified test variables. The aim of covering the samples was to reduce the loss of water due to excessive evaporation during curing at an elevated temperature. The samples removed from the oven after specified curing time temperature and kept in the molds for 5-6 hours in order to avoid drastic changes of the environment. The specimens then removed from the molds left to air dry at room temperature until the specified age test.

5.2 Design Mixes

Tables (3) & (4) represent normal and geopolymer concrete mixes respectively.

Table 3: Normal concrete mixes

Mi. No.	Coarse aggregate Kg/m3			Fine Agg.	cement	W/C	curing	Slump mm	f´c MPa	
	12.5 mm	10 mm	5 mm						7 day	28 day
N.C1	300	400	495	670	400	0.36	water	6	30.7	43.6
N.C2	300	400	495	670	400	0.4	water	15	28.7	42.4
N.C3	300	400	495	670	400	0.45	water	48	27.1	40.8

Table 4: Geopolymer concrete mixes

Consisting		G.C1	G.C2	G.C3	G.C4
Coarse aggregate	12.5mm 10mm 5mm	300 400 495	300 400 495	300 400 495	300 400 495
Sand		670	670	670	670
Fly ash		400	400	400	400
NaOH		41	41	41	51
(M)		8	8	8	8
Na_2SiO_3		103	103	103	129
S/H		2.5	2.5	2.5	2.5
A/F		0.36	0.36	0.36	0.45
S.P		1.5%	1.5%	1.5%	1.5%
E-w		40	30	20	-----
R.P		1hr	1hr	1hr	1hr
Curing T.		70◦C	70◦C	70◦C	70◦C
Slump		196	172	69	44
f'c at 7day		22.2	22.9	29.0	38.1
f'c at 28day		22.3	23.9	30.7	38.8

M: Molarity of NaOH solution, S/H: Sodium silicate solution/sodium hydroxide solution
A/L: Alkaline liquid /fly ash, E-w: Extra water, R.P: Rest period, S.P: Superplasticizer

5.3 Mechnaical Properties of Geopolymer Concrete

The mechanical properties of geopolymer concrete include of compressive strength test was determined according to BS 1881 (1989), using 100 mm cubes. This test conducted for normal and geopolymer concrete at 7 & 28 days. Figures (1) & (2) represent pattern of failure for normal concrete and geopolymer concrete respectively. Splitting tensile strength test is carried out according to ASTM C 496 (2004), cylinder of (100x200) mm. Figure (3) represent splitting tensile strength for geopolymer concrete. It is calculated as follows:

$$f_t = (2P) / (\pi DL) \quad (1)$$

Where: f_t: Splitting tensile strength (MPa), *p:* Applied load at failure (N), D: Diameter of cylinder specimen (mm), *L:* Length of cylinder specimen (mm)

Bonding strength conducted according to RILEM RC6 (1996), cubic specimen having (150×150×150) mm. The that used in this test has the diameter (16) mm and the embedment was (150)mm. Figures (4) & (5) represent the machine of the test and the details of the specimens after test for normal and geopolymer concrete. The bonding strength (τ) is calculated by dividing the tensile force by the surface area of the steel bar embedded in concrete as follow

$$\tau = F/(\pi \times d \times L) \qquad (2)$$

Where:- F: tensile load at failure (N), d & L: diameter (mm) and embedment length (mm) of the reinforcing steel bar respectively.

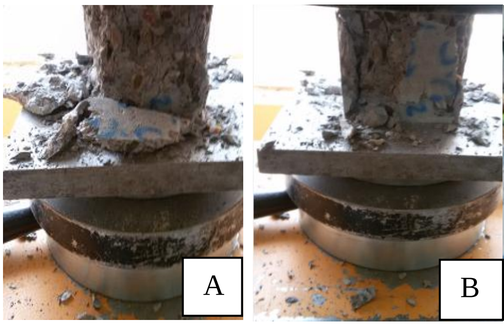


Figure 1: (a) & (b) Pattern of failure for N.C

Figure 2: Pattern of failure for for G.P.C

Figure 3: Splitting strength for G.P.C

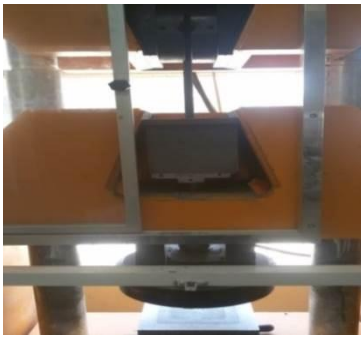


Figure 4: Pullout test machine

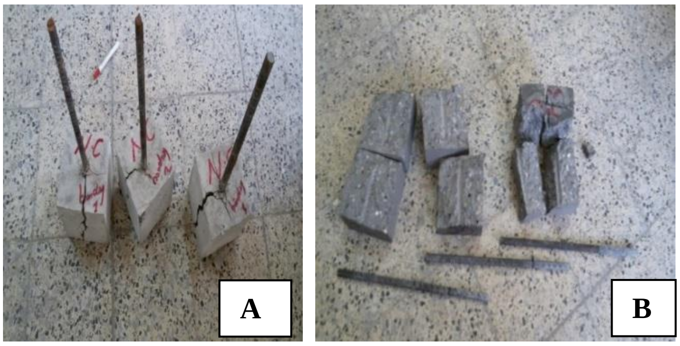


Figure 5: A) N.C & B) G.P.C failures due to bond test

5.4 Durability of Geopolymer Concrete

5.4.1 Permeability Test

The scope of this test is to be measured the depth of penetration of water under pressure of concrete hardening, according to the BS EN 12390 standard (2000). This test was carried out for geopolymer and normal concrete by the of use three samples (150×150×150) mm cube size. As shown in figures (6) & (7) the maximum depth of penetration measure in mm. Permeability coefficient can be calculated from the equation (3) as follow:

$$K = L / T \qquad (3)$$

Where :-K : Permeability Coefficient in mm/sec , L : Length in mm & T : Time in sec

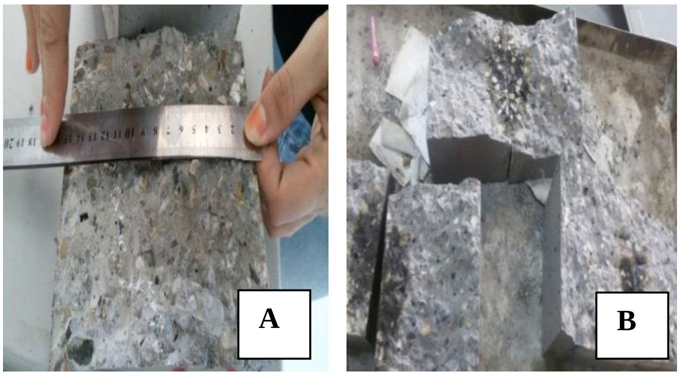


Figure 5: Permeability test machine   Figure 6: (a) N.C & (b) G.P.C Permeability after test

5.4.2 Water Absorption

Water absorption test is conducted according to the specification ASTM C642 (2004). Three samples for each type of concrete. Water absorption was calculated as follow:

$$Water\ Absorption\ \% = [(B - A) / A] \times 100 \qquad (4)$$

where: A: Oven dry mass at a temperature of 105°C for not less than 24 h.

B: Saturated mass after immersing the specimen in water for not less than 48 h.

5.4.3 Sulphate Resistance Test

After 28 days the samples of geopolymer and normal concrete have been put in sulphate solution. $MgSO_4.7H_2O$ was the type sulphate that used in this study. The time of exposure of samples to the sulphate solution was 28 days.Figures(8) & (9) show the samples during and after exposure to sulphate solution in addition to that figure (10) represent the all samples of this study. The visual appearance, change in weight and the residual compressive strength were measured, the change in weight compute as follow:

$$Change\ In\ Weight\ (\%) = [(B-A)/A] \times 100 \qquad (5)$$

where:-

A:Initial weight of sample after curing period & B :weight of specimen after exposure

While the change in compressive strength was calculated as a residual compressive strength based on the following formula:-

$$Residual\ Compressive\ Strength\ (\%) = [D/C] \times 100 \qquad (6)$$

where:-

C: Initial compressive strength ay age of 28 days & D: Compressive strength after exposure



Figure 8: Sample during exposure

Figure 9: Samples after exposure

Figure 10: Sample of this study

5.5 Microstructure of Geopolymer and Normal Concrete Using Sem Test

Figure (11) represents machine of SEM test Its name VEGA III ,TESCAN. The test is conducted in the labs of Ministry of Science and Technology in Iraq

Figure 11: SEM machine

6. Results and Discussions

Normal concrete mix NO. 3 is selected with Geopolymer concrete mix NO. 4 to work all the tests among other mixes because these two mixes are equivalent in compressive strength at 28 days age.

6.1 Mechanical Properties

Geopolymer concrete attain most of its strength at early age usually 7 days (Davidovits, 1994). Test results show that the For 7 days the compressive strength was 98% from the 28 age test, while in normal concrete the 7 days compressive strength were 66.4%from 28 days compressive strength as shown in tables (3) , (4) and in figure (12). Splitting tensile strength results for normal and geopolymer concrete at 7 & 28 days as shown in table (5). It’s shown that geopolymer concrete splitting tensile strenghth at 7 days represent 90.2% from its value at 28 days, while in normal concrete at 7 days splitting tensile strength represent 80.9% from its value at 28 days as shown in figure (13).

Table 5: Splitting tensile strength results for normal & geopolymer concrete

Age day	Normal concrete Splitting strength MPa	Geopolymer concrete Splitting strength MPa
7	3.4	3.7
28	4.2	4.1

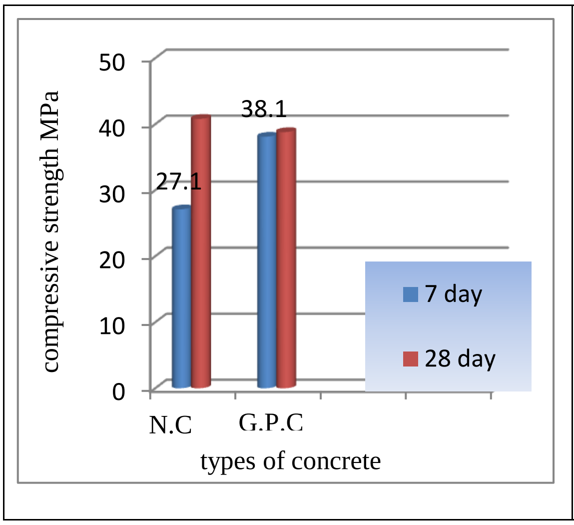


Figure 12: Compressive strength for N.C & G.P.C

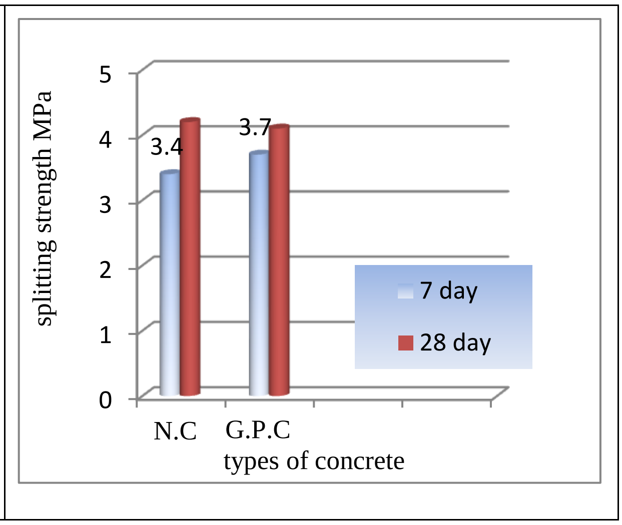


Figure 13: Splitting strength for N.C &G.P.C

Bonding strength test results shown in table (6) noticed that G.P.C bonding strength higher than bonding strength N.C by 18.7%. The higher bonding strength for geopolymer concrete may be attributed to the high bonding between the aggregates and alkaline solution (Doguparti, 2015). Figure (14) illustrates the difference in bonding strength between geopolymer and normal concrete.

Table 6: Bonding strength result for fly ash_ based G.P.C&N.C

Geopolymer concrete				Normal concrete			
P kN at 28 day	Average	τ MPa	Average	P kN at 28 day	Average	τ MPa	Averag
88.38	89.5	11.72	11.87	69.5	76.1	9.2	10
86.82		11.51		80.0		10.6	
93.29		12.4		79.0		10.4	

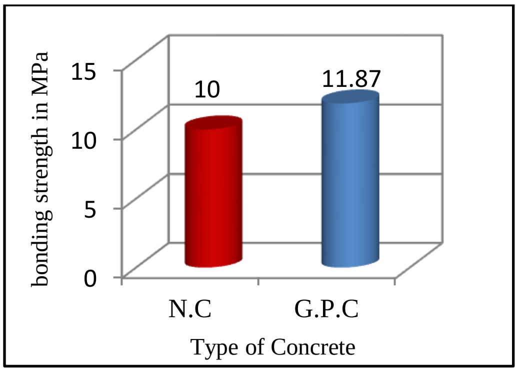


Figure 14: Bonding strength for N.C and G.P.C at 28 day

6.2 Durability Tests

6.2.1 Permeability Test Result

Table (7) shows the test results of permeability for both G.P.C & N.C. From the results it is clear that permeability of geopolymer concrete less than normal concrete by 64.6%. It is due to dense microstructure of geopolymer concrete than normal concrete. Figure (15) shows the difference in permeability for fly ash-based geopolymer concrete and normal concrete.

Table 7: Permeability test results for both G.P.C&N.C

Geopolymer concrete			Normal concrete		
Per. mm	K.coefficient mm/sec	Aver. mm/sec	Per. mm	K.coefficient mm/sec	Aver.. mm/sec
45	1.73×10^{-4}	1.53×10^{-4}	130	5.0×10^{-4}	4.36×10^{-4}
45	1.73×10^{-4}		120	4.62×10^{-4}	
30	1.15×10^{-4}		90	$3.47\times10\text{-}^{4}$	

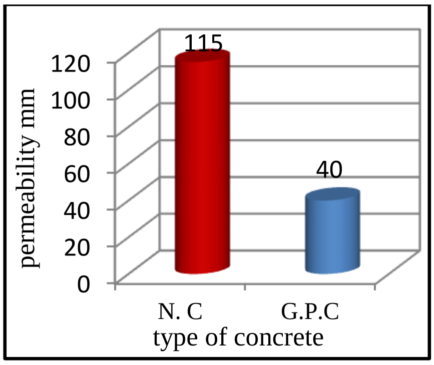


Figure 15: Different in permeability for N.C & G.P.C

6.2.2 Water Absorption Test Results

Water absorption test results for G.P.C & N.C are shown that geopolymer concrete water absorption was less than normal concrete by 38% that is due to less porous nature of G.P.C. because fly ash is fine than O.P.C. (Luhar & Khandelwal, 2015). And according to Nevill (2012) most good concretes have an absorption value well below 10%by mass. Results are shown in table (8) and in figure (16).

Table 8:

Water absorption results for G.P.C & N

Geopolymer concrete		Normal concrete	
Water absorption %	Averag %	Water absorption %	Averag %
2	2	2.6	3.23
1.9		3.4	
2.1		3.7	

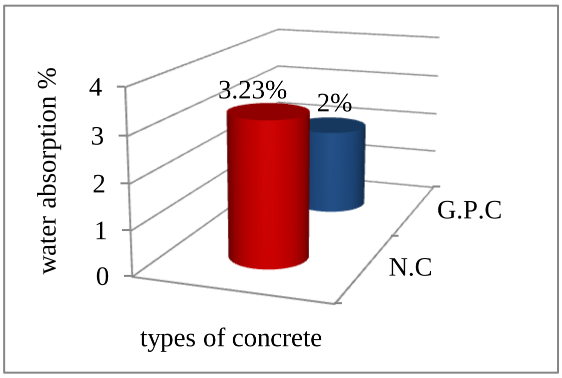


Figure 16: Water absorption for N.C & G.P.C

6.2.3 Sulphate Exposure Test Results

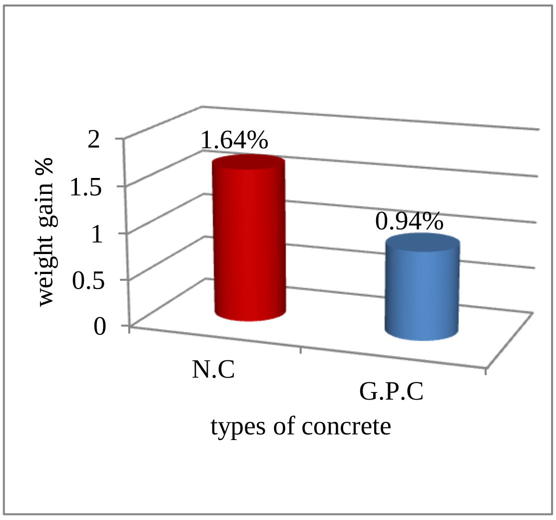
The visual appearance for the surface of samples that exposure to sulphate attack received weight deposits throughout the duration of exposure, these deposits were soft and Powderly as shape flaky or needle at the early age. While the change in weight results are shown in table (9) & in figure (17) these increasing in weight might be due to white deposits within the surface pores (Patil et al., 2014). Table (10) & figure (18) illustrate the results of changes in compressive strength, which refers to decrease in compressive strength for both geopolymer and normal concrete. Ca(OH) that is produced from hydration of cement did not exist in geopolymer concrete for this reason the attack of salts and sulphate is less in geopolymer concrete than in N.C (Mehta & Monteiro, 2006).

Table 9: Weight Gain for the fly ash-based Geopolymer Concrete and Normal Concrete immersed in $MgSO_4.7H_2O$

Geopolymer concrete			Normal concrete		
Sample No.	Wight gain %	Average %	Sample No.	Wight gain%	Average %
1	1.33	0.94	1	1.5	1.64
2	0.85		**2**	1.6	
3	0.64		**3**	1.7	

Table 10: Compressive strength for fly ash _based Geopolymer Concrete at 28 days immersed in MgSO4.7H2O

Geopolymer Concrete				Normal Concrete			
f´c before Expos MPa	f´c after Exposur MPa	F′c Residual %	Change %	f´c befor exposure MPa	f´c after exposure MPa	F′c Residual %	Change %
38.8	36.3	93.5	- 6.4	40.8	35.0	85.7	-14.2
	37.9	97.6	- 2.31		34	83.3	-16.6
	36.2	93.3	- 6.7		35.8	87.7	-12.25



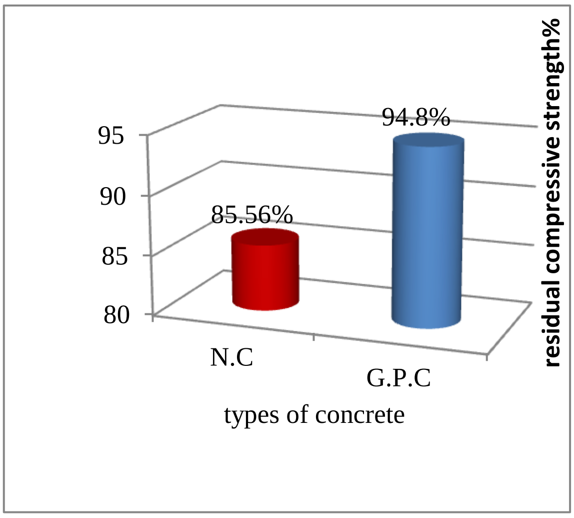
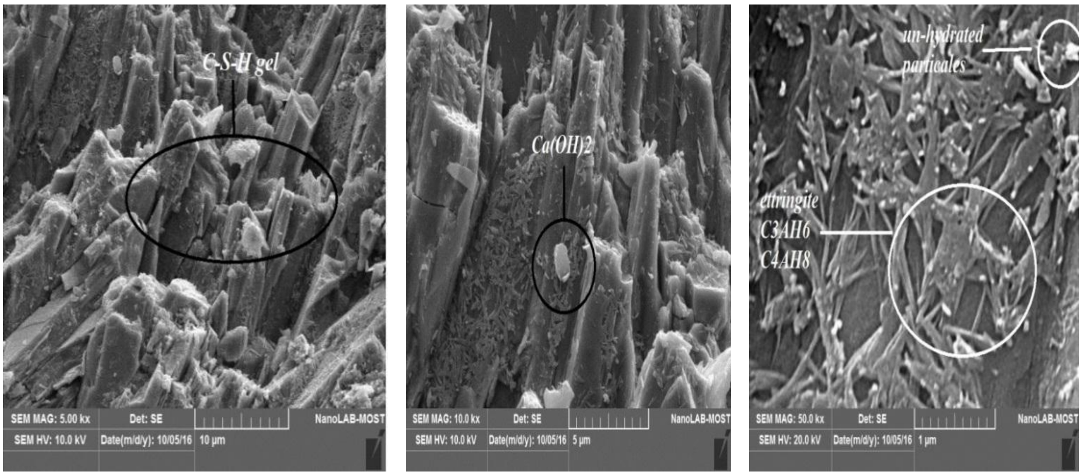


Figure 17: Weight gain for N.C&G.P.C Figure 18: Residual strength for N.C& G.P.C

6.3 Microstructure of Normal and Fly Ash-Based Geopolymer Concrete Using Sem Test

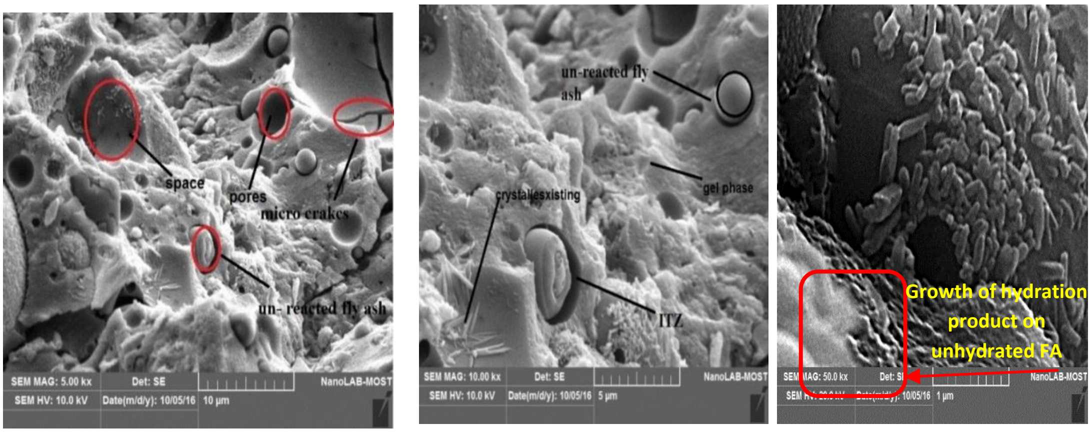
N.C SEM test results are illustrated in figure (19). Figure (19)a with magnification 5000 X explain C-S-H gel (calcium silicate hydrate), figure(19)b with magnification10000 X represent $Ca(OH)_2$ that considers also gel, which results from the hydration of the silicate in cement and because of its shape roofing hexagon cause weakness in resisting cement paste and the last picture(19)c with magnification 50000 explain calcium sulphote aluminate or etrringite (C_3AH_6 ,C_4AH_8) that represents from hydration of aluminate in cement that takes the shape needle and prism shape, the un-hydrated particle of cement seem clear white point.



A) magnification 5000X B) magnification10000X C) magnification 50000X

Figure 19: SEM test results of normal concrete

Figure (20) illustrates geopolymer concrete SEM test results, with magnification 5000X infigure (20)a show spaces, pores, micro cracks appeared in clear shape due to loading during compressive strength or because shrinkage due to the water evaporation during the curing ,as well un –reacted fly ash particles can be observed. In figure (20) b that has the magnification 10000 X can notice crystallesxisting (needle shape particles) these consist because the concentration of sodium hydroxide orabundant alkali solution surrounded the fly ash particles in the geopolymer paste, the unreacted alkali precipitated formed the needle shape particles. Also the figure show gel phase and ITZ between fly ash particles and the gel. Also fig.(20)c shows the growth of hydration product on un-hydrated fly ash particle.



(a) magnification 5000X (b) magnification10000X C) magnification 50000X

Figure 20: SEM test results of geopolymer concrete

7. Conclusion

(1) The G.P.C mixes can be produced easily as alternative materials of concrete, also using the same tools that are used in normal concrete
(2) Higher sustainability achievement can be acquired from fly ash _based G.P.C rather than O.P.C, because the resistance of durability tests of G.P.C is more than N.C
(3) Compressive strength of geopolymer concrete at early age is more higher than normal concrete, it is equivalent to approximately 1.4 to normal concrete compressive strength, because of enhancement in physical properties of geopolymer concrete ingredient such as the finesses, and including the pozzolanic materials.

Splitting tensile strength for G.P.C higher than N.C at age 7 days by 8.8% .

(4) Geopolymer concrete can be used as a construction material, because it have a good compressive strength in addition other mechanical properties.
(5) G.P.C has a higher bonding strength of reinforcement than N.C it is higher by 18.7% than normal concrete, therefore it can be used in reinforced sections and members.
(6) Fly ash _based G.PC compressive strength increase with decrease of the extra-water.
(7) Geopolymer concrete shows dense microstructure and this explain the less water absorption and permeability than normal concrete by 38% and 64.6% respectively.
(8) SEM test studied showed that the morphology of fly ash geopolymer gel contain un-reacted fly ash particles, micro cracks and pores embedded in a continuous matrix, but it is show that micro structure of G.P.C more dense than N.CUSIONS

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